The 2015 World Congress on
Aeronautics, Nano, Bio, Robotics, and Energy (ANBRE15)
Incheon, Korea, August 25-28, 2015

Oxygen and Nitrogen Surface Catalytic Recombination on Copper Oxide in Tertiary Gas Mixtures

Timmy M. Cheung[1)], Gisu Park[2)], and Ferry F. J. Schrijer[3)]

[1), 3)] Faculty of Aerospace Engineering, TU Delft, 2629 HS Delft, Netherlands
[2)] Department of Aerospace Engineering, KAIST, Daejeon 305-701, Korea
[2)] gisu82@kaist.ac.kr

ABSTRACT

Experimentally measured oxygen and nitrogen surface catalytic recombination efficiencies on copper oxide in tertiary gas mixtures are presented. Heat transfer rates at the stagnation point of a blunt body are measured in a shock tube using a thin-film gauge. The measurements were taken at near room temperature using a smooth wall. The heat transfer rates are compared with the theory to obtain the catalytic efficiency. With the oxygen, the efficiency of copper oxide is deduced to be 0.0026 to 0.0032. With the nitrogen, the efficiency is 0.00061 to 0.0014.

1. INTRODUCTION

It is well known that surface catalytic phenomenon causes a considerable increase in the surface heat transfer. At present, a considerable amount of experimental data exists on the catalytic phenomenon for oxygen and nitrogen for practical heat-shield materials. Typically, this data is collected in arc-jet wind tunnels.

Furthermore, the catalytic phenomenon is used also in the characterization of arc-jet tunnels. In these facilities, the average freestream flow enthalpy can be determined by dividing the power input to the gas by the mass flow rate. Although this works as a measure for the average, the enthalpy is higher than the average enthalpy along the centerline of the nozzle flow and lower towards the nozzle wall. Therefore, in general, the enthalpy along the centerline where the material test samples are placed is unknown. A standard procedure to determine this centerline enthalpy is by using a copper calorimeter. Copper is known as a highly catalytic material and its catalytic efficiency is well documented in the literature. Then, the local flow enthalpy is deduced using Goulard's heat transfer formula (Park (2013)), where the measured heat transfer rates from the calorimeter and catalytic efficiency are used as input.

Uncertainties may arise in determining the enthalpy using this approach, because the surface of copper calorimeters becomes oxidized (forming copper oxide) by the oxygen atoms it collided with. The catalytic efficiency of a copper surface deteriorates very quickly once it is exposed to a dissociated oxygen stream. The efficiency is

---

[1)] Graduate Student
[2)] Assistant Professor
[3)] Assistant Professor

defined as the ratio of the number of atoms recombining on a surface per unit area and time to the total number of atoms striking the surface per unit area and time.

Furthermore an additional uncertainty arises about how rough the copper oxide surface is: the rougher the surface, the larger becomes the effective catalytic efficiency. A prolonged exposure of a copper surface may not only oxidize the surface but also roughen the surface. To determine the catalytic efficiency of such a rough surface, one needs first to know the value for a smooth surface. The catalytic efficiency of the smooth copper oxide surface therefore serves as the datum point. To date, a number of studies have measured the copper oxide efficiency using different test facilities. Table 1 summarizes the existing data of catalytic efficiency for copper (Cu) and copper oxide. The copper can be oxidized in two different types of copper oxide: cupric oxide (CuO) and cuprous oxide (Cu_2O).

Table. 1 Summary of surface catalytic efficiency for copper and copper oxide (after Cheung et al. (2015)).

Catalytic efficiency			Test gas	T_w [K]	Facility	Reference
γ_{Cu}	γ_{CuO}	γ_{Cu2O}				
0.17	0.02	-	O_2	300	Side-arm reactor	Greaves & Linnett, 1958
-	0.043	-	O_2	300	Side-arm reactor	Greaves & Linnett, 1959
-	0.045	0.11	O_2	300	Side-arm reactor	Dickens & Sutcliffe, 1964
0.15	-	-	O_2	300	Glow discharge tube	Hartunian et al., 1965
0.063	-	-	O_2	300	Effusion tube	May & Linnett, 1967
0.015	-	-	O_2	300	Diffusion tube	Melin & Madix, 1971
-	-	0.025	O_2	313	Side-arm reactor	Cauquot et al., 1998
-	0.01	-	O_2	300	Side-arm reactor	Nawaz et al., 2013
0.03	-	-	N_2	314	Diffusion tube	Prok, 1961
0.07	-	-	N_2	300	Glow discharge tube	Hartunian et al., 1965
0.08	-	-	N_2	350	Arc-jet	Pope, 1968
0.068	-	-	N_2	300	Side-arm reactor	Rahman & Linnett, 1971
0.10	-	-	N_2	500	Arc-jet	Anderson, 1973
0.40	-	-	N_2	1000	Arc-jet	Anderson, 1973
0.03	-	-	Air	350	Arc-jet	Pope, 1968
0.01	-	-	Air	480	Arc-jet	Park et al., 2006
-	0.01-0.03	-	Air	573	Arc-jet	Nawaz et al., 2013

In Table 1 a summary of surface catalytic efficiency data are given. As can be seen, most of the data are obtained using side-arm reactors, diffusion tubes, or arc-jet facilities. Regarding the side-arm or the diffusion tube, it is known that the accuracy of the methods deteriorates at high catalytic values. The methods are well-suited for low catalytic testing such as ceramics. At present, the copper oxide efficiency has never been measured in a well-defined environment, i.e., in an environment where the flow enthalpy is known independently, the material is unmistakably copper oxide, and the surface is smooth. The surface needs to be exposed to the flow for only a short time in order to prevent roughening. Such a well-defined experiment can best be performed in a shock tube, where the enthalpy of the flow is known from the shock speed.

In 2013, therefore, for the first time, the present author has measured catalytic efficiency of copper oxide as well as copper surfaces using a heat transfer gauge in a shock tube using oxygen flows (Park (2013)). The work was then continued on nitrogen flows (Cheung et al. (2015)). From these studies, it was found that the copper oxide efficiencies for the oxygen flows are about one order of magnitude smaller than that of the copper. Nitrogen data showed a similar trend.

2. DETERMINATION OF CATALYTIC EFFICIENCY

The experiments were conducted in a shock tube located in the department of aerospace engineering at KAIST. Two test gases, oxygen and nitrogen, were considered. For the oxygen case, a mixture of 21 % oxygen and 79 % argon by volume was used. For the nitrogen, a mixture of 35 % nitrogen and 65 % krypton was used. Various flow conditions were considered having either oxygen or nitrogen dissociation.

A flat-disk cylinder model was used, which had an outer diameter of 12 mm. A platinum thin-film gauge was used for heat transfer rate measurements. One heat transfer gauge was flush mounted at a time at the model center. The surface of the model was coated with silicon dioxide (SiO_2), copper oxide (CuO or Cu_2O), or copper (Cu). The SiO_2 layer (known as non-catalytic) was used as an intermediate layer (electrical insulator) between the platinum thin-film and the copper oxide or copper.

The surface catalytic efficiencies were determined by finding intersection points between the measured and the calculated heat transfer rates. The calculations were made using the theory based on hypersonic approximation. Catalytic efficiency was one of the main inputs to the theory. Full details of the theory are given in Park (2013).

3. RESULTS AND DISCUSSION

Figure 1 presents the measured oxygen and nitrogen surface catalytic efficiencies (γ_w) for copper and copper oxide from various sources including the present data. A distinction is made between the Cu (denoted by the open symbols), the CuO (filled squares), and the Cu_2O (gray filled stars). The symbol T_w denotes wall temperature. In this work, the T_w was obtained by averaging the temperature measured by the thin-film gauge during steady flow conditions.

Concerning the oxygen, the γ_w for the copper is about a factor of 6 higher than that of the copper oxide. For both the copper and the copper oxide data, the present values are much lower than the existing data. Because the existing data were obtained using the side-arm or diffusion tube facilities in which efficiencies were determined in a very different way, making direct comparisons between the two approaches difficult. As mentioned, it is known that the accuracy of the side-arm method deteriorates at high catalytic values.

Concerning the nitrogen, the γ_w for the copper is about a factor of 28 higher than that of the copper oxide. For both the copper and the copper oxide data, the present values are in general lower than the existing data. Looking at the data of Anderson, for example, the γ_w for the copper is about a factor of 4 to 14 higher than the present data. This is thought to be due to high wall temperature along with rough surface induced during the arc-jet testing (Park (2013)). Comparing the nitrogen efficiency for the copper oxide with that of the oxygen, the nitrogen value is about a factor of 3 smaller than that of the oxygen.

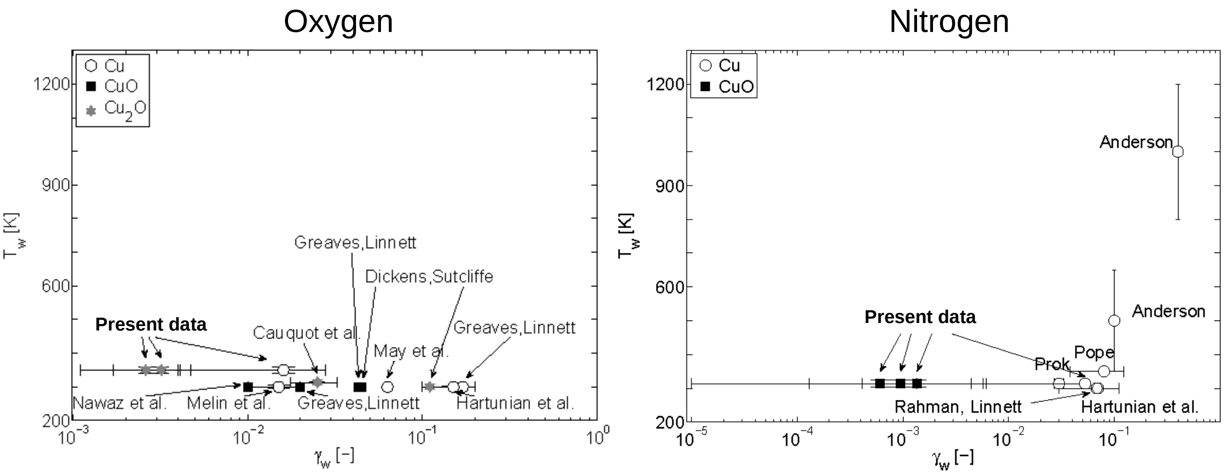

Fig. 1 Variation of surface catalytic efficiency with wall temperature
(after Cheung et al. (2015)).

4. CONCLUSIONS

Stagnation-point heat transfer experiments were conducted using the shock tube. Oxygen and nitrogen flows were considered respectively. With the oxygen case, catalytic efficiency of copper oxide is deduced to be 0.0026 to 0.0032, while copper has an efficiency of 0.016. With the nitrogen case, catalytic efficiency of copper oxide is deduced to be 0.00061 to 0.0014, while copper has an efficiency between 0.0031 and 0.053.

REFERENCES

Gisu Park (2013), "Oxygen Catalytic Recombination on Copper Oxide in Tertiary Gas Mixtures", *J. Spacecraft and Rockets,* **50**(3), 540-555.

Timmy M. Cheung, Gisu Park, and Ferry F. J. Schrijer (2015), "Nitrogen Catalytic Recombination on Copper Oxide in Tertiary Gas Mixtures", to be submitted to *J. Spacecraft and Rockets,* 2015.